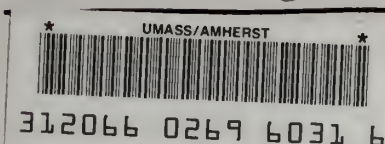
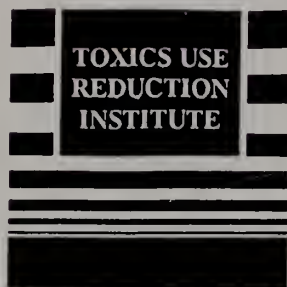


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CRANSTON PRINT WORKS
WEBSTER, MASSACHUSETTS

TOXICS USE REDUCTION
THROUGH PROCESS IMPROVEMENT,
SUBSTITUTION & INTEGRAL RECYCLING

TOXICS USE REDUCTION INSTITUTE
CLEANER TECHNOLOGY
DEMONSTRATION SITES PROGRAM

Cranston Print Works, Webster, Massachusetts

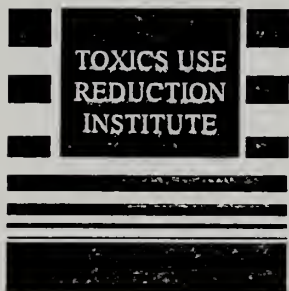
Toxics Use Reduction Through Process Improvement, Substitution & Integral Recycling

**Mark V. O'Brien, Project Manager
Cranston Print Works**

The Toxics Use Reduction Institute Cleaner Technology Demonstration Sites Program

**The Toxics Use Reduction Institute
University of Massachusetts Lowell**

1996



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The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854.

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Preface

In its 1996 fiscal year, the Massachusetts Toxics Use Reduction Institute launched the first Cleaner Technology Demonstration Sites Program. The goal of the program was to promote the adoption of cleaner technologies by Massachusetts industry. Five companies were selected as demonstration sites to showcase the implementation of technologies that embrace the concepts and principles of toxics use reduction. The program, which included a series of visits to the facilities and related presentations and publications, allowed individuals and firms to observe and assess their value first-hand. Site visits were open to industry, environmental groups, community groups, the media and others.

Associate sponsors of the program included the Massachusetts Office of Technical Assistance for Toxics Use Reduction, the Executive Office of Environmental Affairs, the Department of Environmental Protection, the Environmental Protection Agency of New England, and the Associated Industries of Massachusetts.

This was the first of an annual program allowing a broad range of companies to showcase cleaner technologies. The program will continue to provide grants to recognize the many companies across the Commonwealth that have used toxics use reduction and cleaner technologies while enhancing their firm's competitiveness.

The following report is an in-depth analysis of the cleaner technology(ies) demonstrated at Cranston Print Works, Webster, Massachusetts.

Notice

This report has been reviewed by the Institute and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Toxics Use Reduction Institute, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.



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1.0 INTRODUCTION

1.1 Project Intent

With the goals of toxics use reduction (TUR) and pollution prevention, Cranston Print Works Company has developed innovative technologies and methodologies for traditional textile processes. The focus of some of these efforts is the reduction in the use of acetic acid and sulfuric acid at Cranston's Webster, Massachusetts facility.

In order to reduce cost, worker exposure to hazardous materials, and environmental impact, Cranston Print Works has implemented programs involving the TUR techniques of process modernization, in-process recycling and operations improvements. In-process recycling for an acid ager incorporated integral acetic acid recycling in the process. Control charting and automation of the process to monitor and regulate the use of acetic acid has resulted in significant reductions through process modification and operations improvements. Input substitution for end-of-pipe treatment has also been implemented, using carbon dioxide to replace sulfuric acid as a means of treating alkaline waste in the on-site wastewater treatment facility.

1.2 Description of Cranston Print Works

Cranston Print Works Company started printing cotton cloth in Cranston, RI in 1824. Operations were expanded to include the current Webster, MA site in 1936 with the purchase of the historic Slater East Village Mill where Samuel Slater had developed the first American cotton-spinning machinery. Printing operations were again expanded with the acquisition of another division in Fletcher, North Carolina. Currently, the Webster division provides preparation, printing, and finishing of cotton and polyester/cotton blended fabrics.

Cranston Print Works operates under SIC codes 2261 and 2262 and reports on several chemicals under the Massachusetts Toxics Use Reduction Act (TURA). Cranston's use of azoic dyes requires an acid aging process which results in the use of reportable quantities of acetic acid. They also use enough alkaline chemicals to require substantial use of pH neutralizing agents.

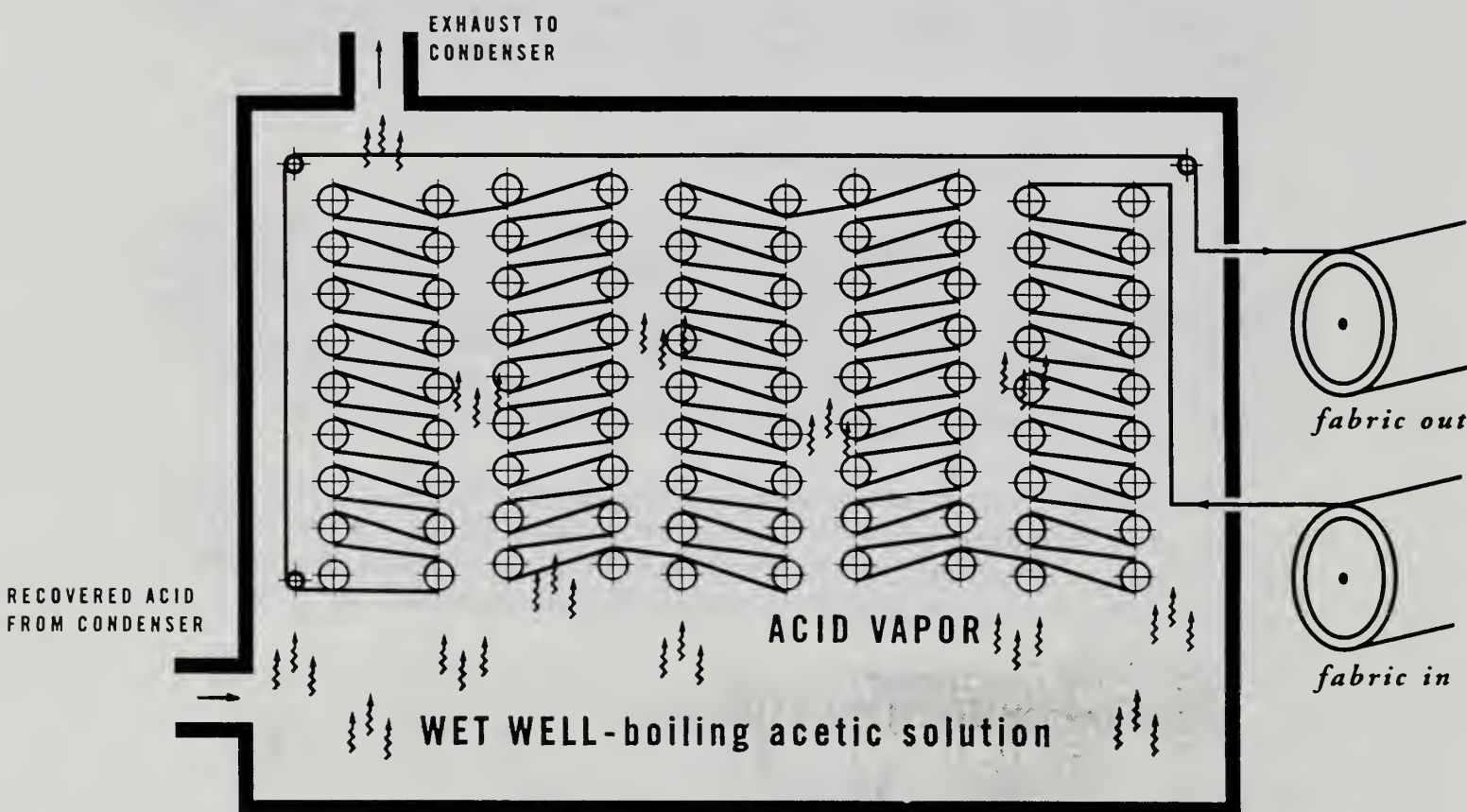
2.0 DESCRIPTION OF TECHNOLOGIES

2.1 In-Process Acid Vapor Recovery

After printing with azoic, or naphthol, dyes, the printed fabric must be exposed to an acid environment to react the dye molecules so that the desired color is achieved. Azoic dyes consist of two components when applied to the fabric, the first of which is an aromatic diazo molecule that bonds to the fabric. The second component is a diazonium salt, which will only

bond with the diazo molecule to form the desired, brilliant shade when exposed to an acid environment. This exposure of the dyed textile to an acidic vapor is known as "acid aging".

The acetic acid used to bond the two components of the azoic dyes is delivered as a vapor to the printed textile through the use of a heated acid bath. The bath, a 5% acetic acid solution, is kept at 215°F in a vessel called an ager through which 267 yards of fabric is laced on rollers. The fabric, upon entering the ager, passes over a series of rollers at a speed of approximately 150 yards per minute which provides the appropriate residence time (1.5-2.0 minutes) for the reaction to occur. In a reservoir, or wet well, at the bottom of the ager, the acid solution is boiled, producing the vapor to which the fabric is exposed (Figure 1). Approximately 4% of the acid is either consumed in the dye chemical reaction or remains as residue on the textile to be washed off in a subsequent operation. The 96% balance of the acid vapor in the ager escapes the vessel and is captured in an exhaust system.



- Exposure to acidic acid environment binds the two parts of the azoic dye, resulting in brilliant reds and rich blacks.

Figure 1 - Acid Aging

The fate of the acid steam exhaust from the two pre-existing agers, which once handled the entire plant's azoic capacity, follows the schematic illustrated in Figure 2. The acid steam passes through a scrubber which is provided with 56 gal/min of fresh water. Since acetic acid is highly soluble in water, it is absorbed by the water in the scrubber, which is sent to wastewater treatment while the cleaned air stream is emitted at the stack.

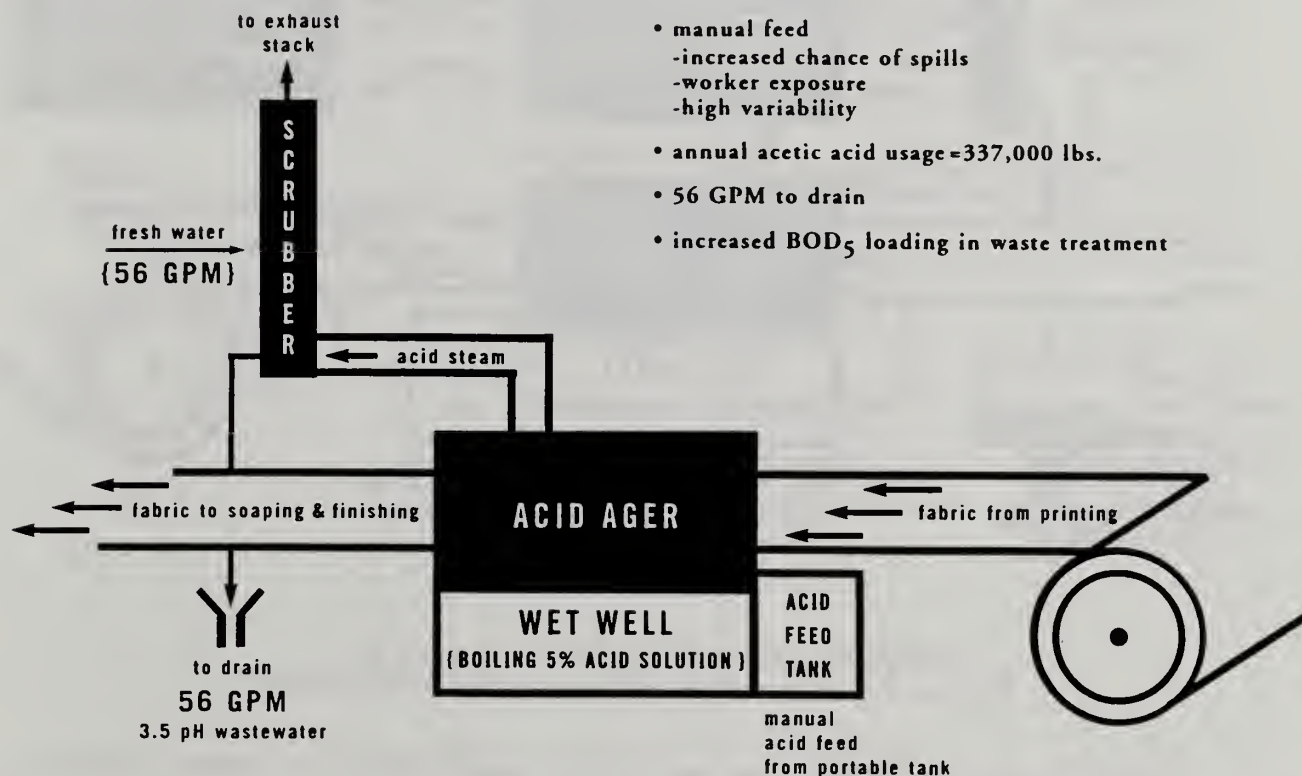


Figure 2 - Acid Aging Without Acid Recovery

The new, third ager, which has picked up 77% of the plant's azoic dyeing capacity, incorporates integral acid recovery and scrubber water recirculation into the process flow as illustrated in Figure 3. The acidic steam exhaust from the ager passes into a condenser which uses 44°F chilled water to condense the acid/steam mixture in the chamber. Ninety percent of the acetic acid and 98% of the water vapor in the exhaust stream is recovered in this condensation process. The condensed acid/water stream is piped directly back to the wet well of the ager for reuse as acidic steam in subsequent operations. Fresh acid solution is added to the wet well to make up for the 10% in losses.

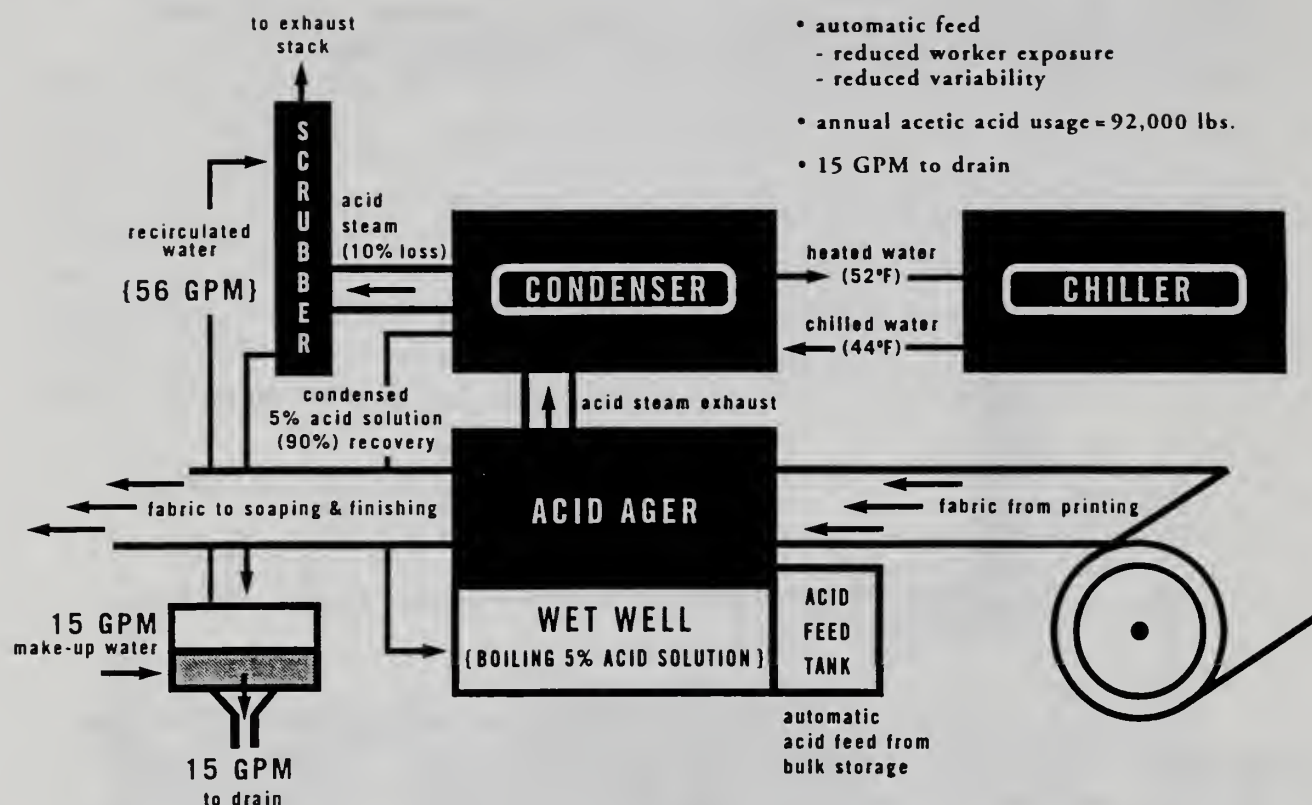


Figure 3 - Acid Aging With Integral Acid Recovery

The 10% balance of the steam and acid is then passed through the scrubber. Due to the reduction of the acid content in this exhaust by 90% (as compared to the original process) and the heat loss in the condenser (due to heat exchange from the acid steam to the 44°F chilled water stream), the scrubber water is required to absorb much less acid and heat. As a result of this decreased heat and acid absorption, the scrubber water can be recirculated with the addition of only 15 gal/min of fresh water, while 15 gal/min are drained to wastewater treatment to maintain a constant process volume. The water to drain has been reduced by 73% and is of a much lower acid concentration.

Water used in the chiller to maintain the low temperature of the condenser refrigerant is subject to recirculation as shown in Figure 4. The acid steam is cooled in the condenser, and the warmed water from the condenser is cooled to 44°F in the chiller. The warmed water from the chiller is cooled by ambient air at the roof-mounted cooling tower. This air-cooled water is then routed back to the chiller to complete the closed-loop heat absorption system.

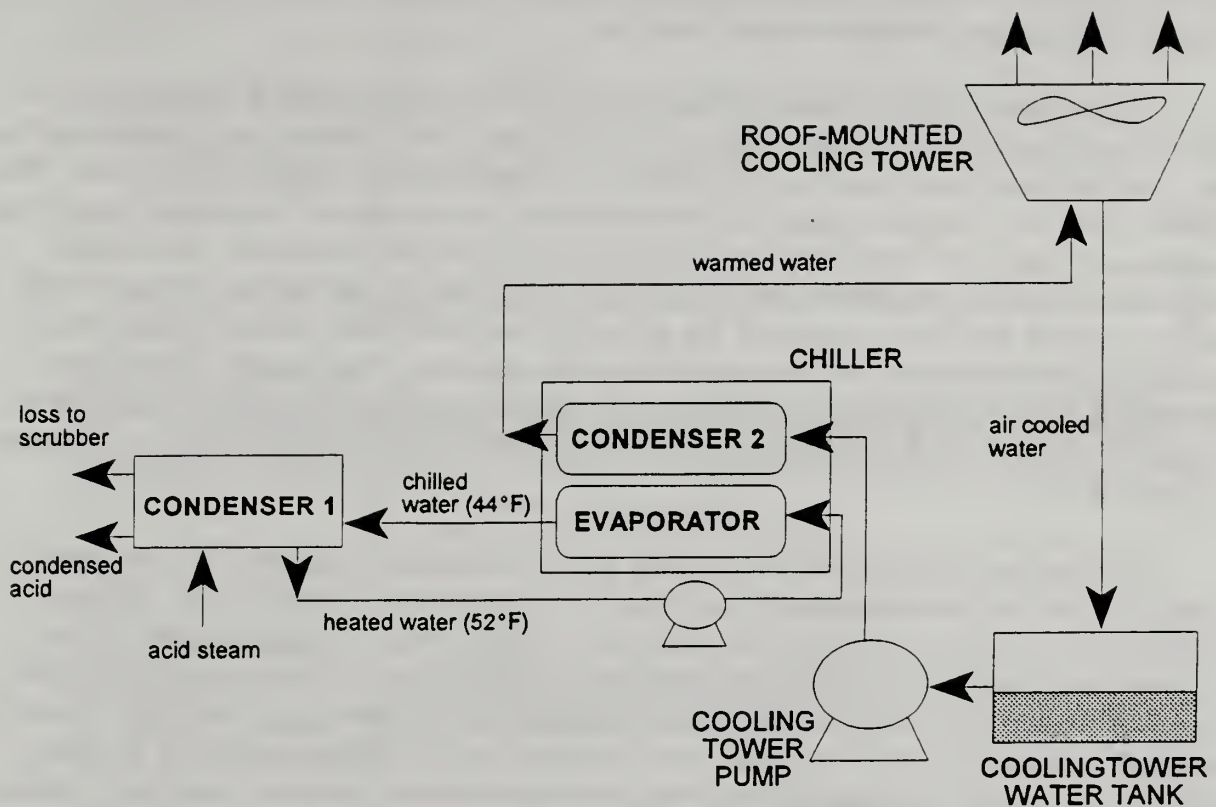


Figure 4 - Chiller Water Recirculation

2.2 Control Charting

As a result of TUR planning and the application of the Deming Quality Process, a multi-disciplinary team consisting of supervisors, management, and engineering personnel sought to use control charting for processes throughout the plant. Control charting is a means of monitoring the state of a process as a function of process inputs by illustrating normal process variability and highlighting extreme disturbances. Analysis of the control chart then allows for study of whether or not the process is "in control" - exhibiting acceptable variability, and highlights costly non-standard occurrences. As the process is improved and non-standard occurrences are eliminated, variability is reduced and tighter control limits are realized.

One area in which they implemented a control charting pilot program was the acid steam aging process. The acid steam agers that were not equipped with in-process acid recycling use control charting to ensure optimum process efficiency, defined here as achievement of highest product quality with minimum use of acetic acid.

The chemical reaction which occurs during the acid aging process is optimal in a 5% acetic acid environment. An environment which exceeds 5% acid introduces excess acid into the process, while an environment of less than 5% acid can result in dye quality issues. Past process control for the acid agers involved the manual adjustment of the metering pump to add acetic acid into the wet well from which the acid/steam mixture is formed. The manual adjustment of this operation resulted in very high variability in wet well acid concentration. In order to ensure high quality product, the amount of acid which was manually added to the system was much higher than the chemical reaction required. The baseline control chart describing this process variability and the mean value of acid concentration is illustrated in Figure 5. Note the range between the upper and lower control limits of 11.3% and the mean value of 6.8%.

The process improvement team, noting this high variability, targeted the acid input component of the acid aging process as in need of improvement. Traditionally, the acid delivery method involved filling a portable tank manually from a bulk storage tank. This portable tank was then brought to the ager where a series of hoses, clamps, and pipes were assembled manually in order to transfer the contents into the ager's acid feed tank. Once a day the acid concentration in the tank was monitored and controlled through regular sampling, titration and manual pump adjustment. This manual addition of the acetic acid was replaced with a Tytronics Model No. 301 automated acid feed in conjunction with the same acid pump. The Tytronics unit intermittently titrates the contents of the wet well to determine percent acetic acid and provides regulatory feedback to the pump to control acid input from the acid feed tank into the wet well. The resulting variability of the process is illustrated by the control chart in Figure 6. Note that the range between the upper and lower control limits has been reduced to 2.4% and the mean has been reduced to 5.7%.

In spite of the significant improvement in controlling acid concentration in the wet well, the team continuously sought to improve the process. They studied the existing variability using the newly calculated upper and lower control limits of the process with the Tytronics unit automatically controlling acid concentration. By noting "out-of-control" data points and identifying their cause, it soon became apparent that the level of the wet well needed to be controlled better. By manually controlling the level, a tendency to overfeed water to insure the well did not run dry was typical. Overfeeding or continuously "overflowing" the wet well, led to excessive acid waste. Automatic level measurement and control was implemented resulting in an average acid concentration of 5.3% with a range of 1.1% (Figure 7). The annual reduction in acid use as a result of overall process improvements from control charting is approximately 128,000 lb.

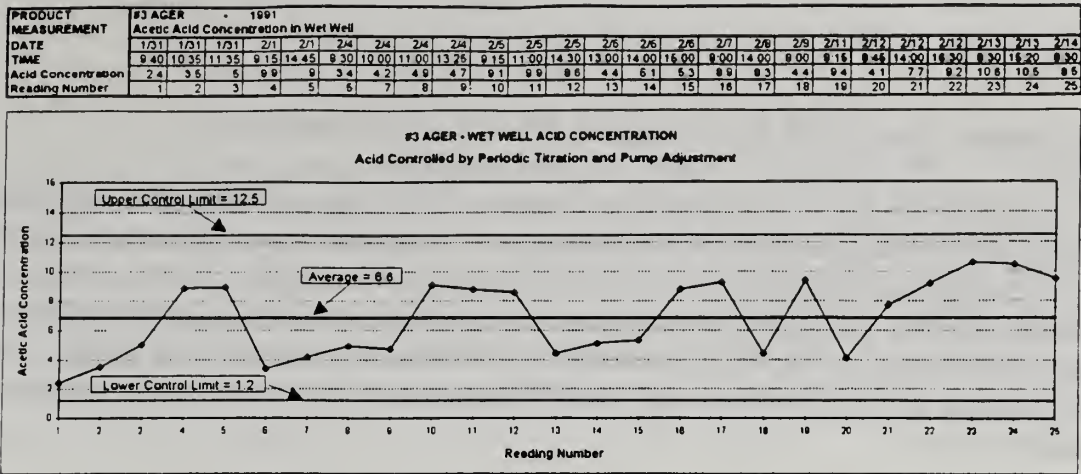


Figure 5 - Statistical Process Control Chart with Manual Control

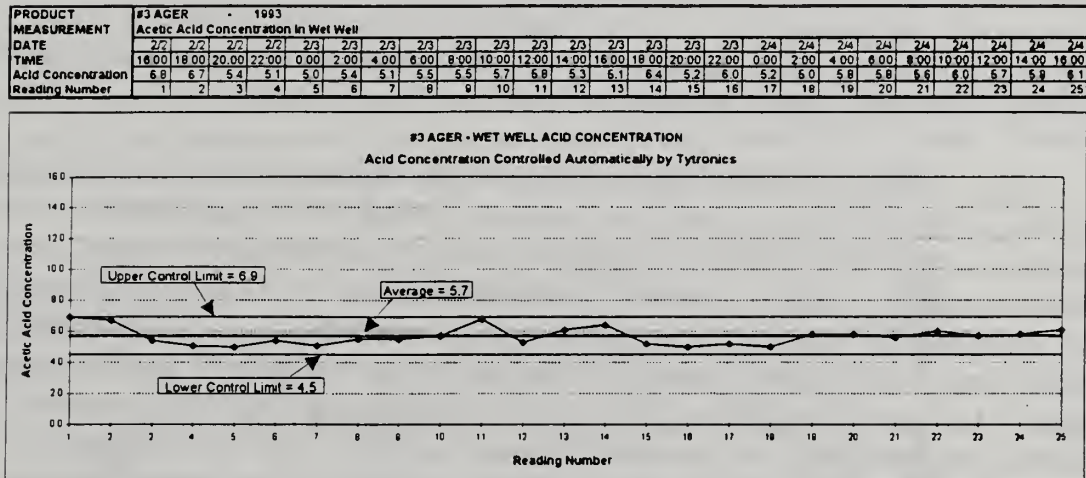


Figure 6 - Statistical Process Control Chart with Tytronic Unit

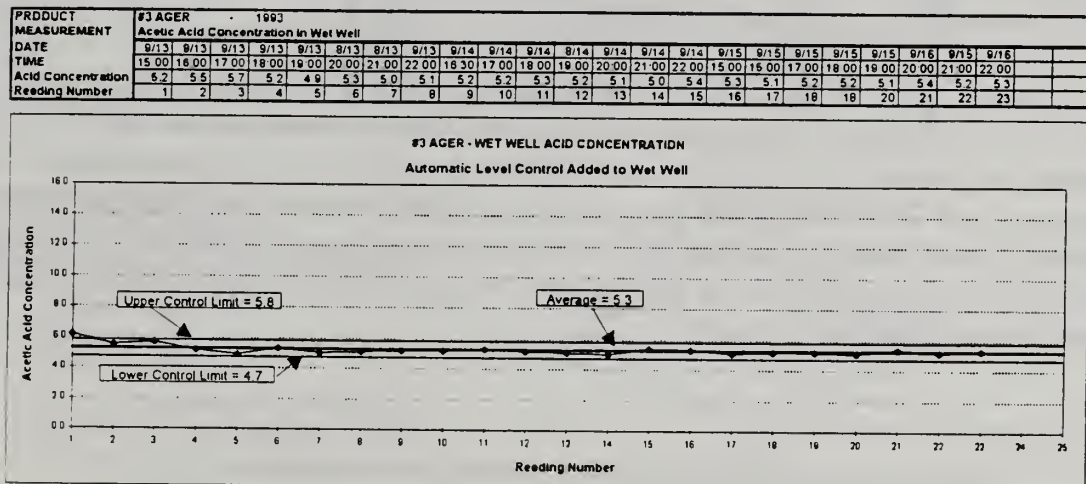


Figure 7 - Statistical Process Control Chart with Level Control

2.3 Carbon Dioxide Substitution in Wastewater Treatment

The substitution of carbon dioxide for sulfuric acid represents another significant achievement by Cranston Print Works resulting in substantial reductions in toxic chemical usage. The application of CO₂ in wastewater treatment in a unique delivery system eliminated Cranston's facility-wide usage of sulfuric acid. Although using CO₂ for the treatment of alkaline wastewater is a technology which is not unique to Cranston Print Works, through TUR planning and good engineering, it was selected as the best option and designed to meet Cranston's needs.

Pre-treatment of textiles prior to the printing process involves repeated exposures to caustic, alkaline solutions to eliminate debris such as lint particles and to prepare the fabric for quality dyeing. As a result, the wastewater stream at Cranston Print Works is generally alkaline, with a pH greater than 11. This alkalinity must be neutralized to a pH of approximately 8 before discharge into the local publicly owned treatment works (POTW). This neutralization was traditionally accomplished with sulfuric acid.

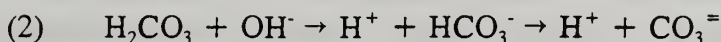
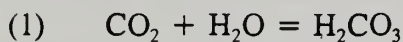
When Cranston Print Works first considered the implementation of a CO₂ system in 1992, two methods of CO₂ delivery were available, in-line delivery and diffusion delivery. In-line delivery, or injecting gaseous CO₂ into wastewater pipes en route to holding tanks, requires a length of piping to allow sufficient residence time for the neutralization reaction to occur. Diffusion delivery is done by bubbling CO₂ through the liquid in a holding basin of sufficient depth to achieve the appropriate residence time. Neither of these methods were practical at Cranston Print Works. The length of pipe necessary for in-line residence time would have been unwieldy and disrupt other plant operations. In order to maintain a constant flow to the POTW as required, the level of the basins dropped during weekends when wastewater was not being generated but constant outflow to the POTW was maintained. This reduction in the level of wastewater in the basins resulted in diminished depth and thus insufficient residence time for the diffusion delivery method.

Cranston Print Works decided to take advantage of the turbulence created by jet aeration headers which combined 15,000 gal/min of recirculated wastewater with 1,000 ft³/min of air to reduce the biochemical oxygen demand (BOD)¹ in each of two treatment basins. Forty nozzles on both 14" liquid header pipes act as aspirators to mix air and wastewater to maintain dissolved oxygen levels and lower BOD₅². Neutralization is accomplished by injecting liquid carbon dioxide through 10 valves directly into the liquid header of both basins. Figure 8 illustrates this piping configuration.

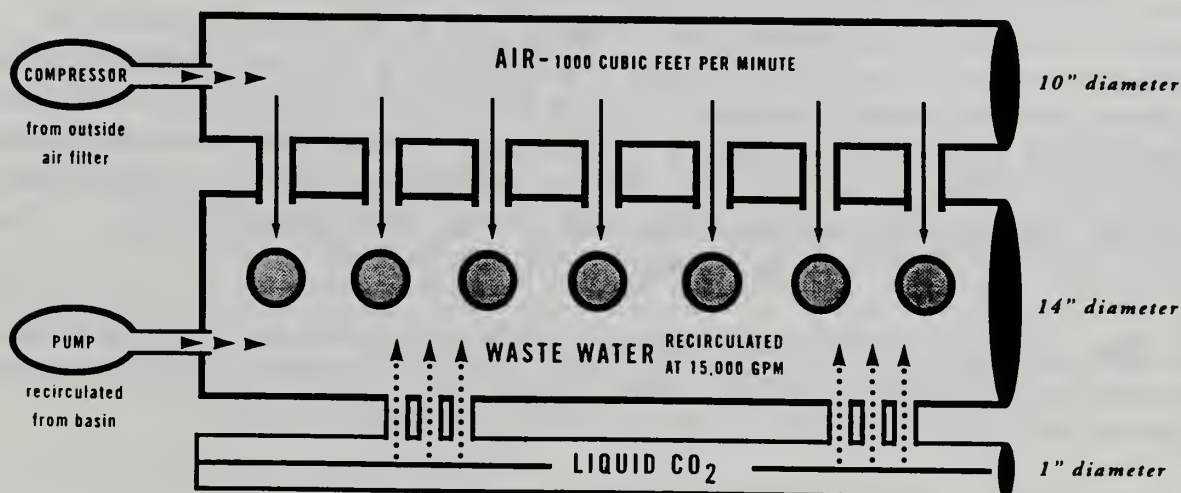
¹ A measure of organic pollution as measured by the oxygen consumption of organic matter.

² The standard measurement of organic pollution as measured by dissolved oxygen consumption by microorganisms in five days.

As the liquid CO₂ leaves the pressurized pipe and enters the liquid header, it converts to a gaseous state. When the gaseous CO₂ is combined with water, it forms carbonic acid, or H₂CO₃, as represented by equation (1). The turbulence created by the jet aeration system further accelerates this chemical conversion, and the excess CO₂ continues to react as it diffuses upwards in the tank thus enhancing the process. As described in equation (2), the H₂CO₃ converts to carbonate species, releasing hydrogen ions (H⁺) into the wastewater. The hydrogen (H⁺) ions react with the hydroxyl (OH⁻) ions present in the alkaline waste stream, and the pH level is thus reduced.



The CO₂ vendor conducted bench-scale tests with Cranston wastewater to ensure the viability of this new process prior to implementation of the production scale unit. These tests determined that liquid CO₂ would be able to meet the neutralization demands.



- need for sulfuric acid substitute noted due to TUR planning
- neutralization alternatives examined
 - organic only
 - organic + acid
 - acid only
 - carbon dioxide only
- unique CO₂ delivery system developed
 - side-stream + basin (diffuser) effect

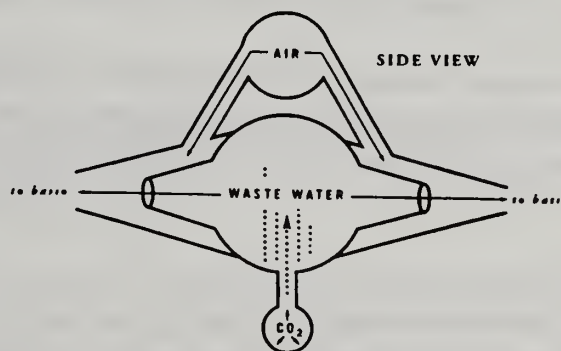


Figure 8 - Carbon Dioxide Delivery System

3.0 ENVIRONMENTAL AND OCCUPATIONAL HEALTH ASSESSMENT

The techniques employed at Cranston Print Works have resulted in significant reduction in the use of acetic and sulfuric acid. Both of these chemicals, especially sulfuric acid, can result in inhalation poisoning or burns to plant personnel depending on the exposure route, dosage, and duration of contact. Accidental release into the environment would have severe adverse effects on those organisms with which the chemicals come into contact. The successful implementation of technologies which lead to the reduction or elimination of these chemicals can significantly reduce the risks they present.

3.1 Acid Vapor Recovery

The implementation of an integral acid vapor recovery system at Cranston has had a positive impact on environment and occupational health and safety.

3.1.1 Environmental Impact

Prior to the installation of the third, higher capacity, ager with its integral acid recycling system, Cranston Print Works' Webster Division annually used approximately 670,000 lb of acetic acid in the acid aging process. Approximately 96% of this acid went to drain for wastewater treatment before discharge to the local POTW along with the 120,000 gallons/day of water which was used in the scrubber to remove the acid from the ager exhaust. With the implementation of the closed-loop ager, acetic acid usage for this production unit decreased to 259,000 lb/yr in 1994 representing a 61% reduction in acetic acid, and to 240,000 lb/yr in 1995. The 1994 Byproduct Reduction Index (BI)³ resulting from these production modifications was 57.7% from the base year of 1990 (see Table 1).

Since acetic acid can be characterized by 0.9 lb BOD/lb acetic acid, the reduction in acetic acid has resulted in a reduction in BOD level by 55%. This BOD reduction is important because of additional POTW costs for the treatment of this organic pollution.

3.1.2 Occupational Health and Safety Impact

The reduced volume of acetic acid used at the plant due to vapor recovery translates to less potential acid exposure for plant personnel. The implementation of an automated acid delivery system for the new ager dramatically reduced worker handling and exposure to acetic acid.

³ BI is calculated according to the formula $100 \times [(A-B) \div A]$, where:

A = byproduct generated in the base year $\div$ unit of product generated in the base year

B = byproduct generated in the reporting year $\div$ unit of product generated in the reporting year

3.2 Control Charting

The implementation of control charting has resulted in the highlighting and correction of processes which were in poor control. The cited example of monitoring the acid feed into the older agers resulted in an awareness of the lack of control from manual acid loading. Installation of the automatic-feed Tytronics unit brought the process into much tighter control and reduced acid handling on the part of the workers. Process improvements resulting from control charting in the acid agers have reduced acetic acid usage by 128,000 lb/yr.

3.3 Carbon Dioxide Wastewater Treatment

Prior to the implementation of the carbon dioxide alkaline neutralization system in Cranston's wastewater treatment facility, the plant consumed 2.66 million pounds of sulfuric acid each year. The Webster Division has totally eliminated the use of sulfuric acid, replacing it with 1 million lb/yr of liquid carbon dioxide (see Table 1). Costly maintenance, worker safety, spill prevention and environmental concerns have been eliminated, including fears of hydrogen sulfide poisoning resulting from the potential chemical reaction of the sulfuric acid.

Table 1
Annual Acid Use and Byproduct (lbs.)

		1988	1989	1990	1991	1992	1993	1994	1995
Acetic Acid	use	NA	662,100	544,000	535,000	512,000	474,000	259,000	240,000
	byproduct	NA	NA	522,000	513,000	491,000	455,000	249,000	230,000
Sulfuric Acid	use	1,429,000	1,627,000	1,862,000	2,661,000	934,000	0	0	0
	byproduct	0	0	0	0	2,545	0	0	0

4.0 ECONOMIC ASSESSMENT

4.1 In-Process Acid Vapor Recovery

The TUR and pollution prevention projects undertaken by Cranston Print Works have had a positive economic impact on the company in addition to the positive impact on the environment and on occupational health and safety.

Reduced operating costs for the acid recovery system have justified the capital expenditure of \$235,000. This capital expenditure includes the costs of the condenser unit, chiller, cooling tower, tanks (2), pumps (4), scrubber and all associated piping and chemical treatment system for the cooling tower to prevent corrosion. The payback period for the

system was approximately one year. The savings realized include reduced acetic acid material costs and reduction in POTW costs for hydraulic flow and BOD treatment. Additional operating costs include water treatment chemicals (primarily corrosion inhibitors and anti-bacterial agents used in the cooling tower) and electricity required to run the pumps, chiller, and condenser. The net monthly savings average approximately \$18,400, with a cost savings per unit of product estimated at \$22 per 1000 lb. of fabric processed. Approximately \$230,000 in net annual savings is added directly to the company's bottom line. Table 2 summarizes the costs incurred and the savings realized as a result of implementation of the acid recovery system.

Table 2
Summary of Savings & Costs for a Typical Month
 (December 1993)
Integral Acetic Acid Recovery

Savings	
Hydraulic Flow to POTW	\$2,943.65
Acetic Acid	\$7,012.94
BOD Treatment at POTW	\$13,635.37
Costs	
Water Treatment Chemicals	(\$253.00)
Electrical	(\$4,924.86)
Net Savings	\$18,414.10

4.2 Control Charting

Measuring the cost impact of control charting is an ongoing process. As identified operational improvements are implemented, the company should continue to realize economic benefits. For the example cited in this report, the annual reduction in acetic acid usage resulting from process improvements translates to an approximate annual material cost reduction of \$33,280. This material savings and the reduction in labor costs have more than justified the approximately \$18,000 capital expenditure for the Tytronics unit. Additional savings from quality improvements and fewer defects have been realized but are difficult to quantify, and thus the full economic benefit of control charting in this process exceeds what actually is measurable.

4.3 Carbon Dioxide Wastewater Treatment

The costs and savings resulting from the implementation of the carbon dioxide wastewater treatment system are outlined in Table 3. Elimination of 2.66 million lb/yr of sulfuric acid saves \$120,000 as compared to the carbon dioxide cost of \$50,300 which translates to a net annual savings of approximately \$70,000. The regulatory compliance fees of \$3,000 have also been eliminated for sulfuric acid usage. The capital expenditure of \$93,000 for the piping, pumps, vaporizer, condenser, control panel and carbon dioxide tank had a payback period of 1.5 yr.

Table 3
Summary of Savings/Costs for a Typical Year (1995)
Carbon Dioxide Treatment of Wastewater

Savings	
Sulfuric Acid	\$120,000
TURA Fees	\$3,000
Costs	
Carbon Dioxide	(\$50,300)
Net Savings	\$72,700

5.0 RESOURCES AND BARRIERS

The TUR and pollution prevention efforts at Cranston Print Works were facilitated by the support of management, the involvement of all levels of the work force in decision-making, and previous successes with TUR.

5.1 Management Support

The mission statement for the Webster Division states that the environment must be respected in all decisions. Management, acting in accordance with this statement, has encouraged and provided financial support for efforts made to minimize environmental impact and occupational exposures. Previous successes with TUR facilitated this support.

5.2 Involvement of Plant Personnel

As part of the TUR planning process, plant personnel at all levels were involved in developing new operating procedures. This involvement assured the buy-in of key individuals, particularly those at the operator/technician level who would be responsible for implementing and using these new procedures. Most plant employees are involved in voluntary action teams to maintain a policy of continuous improvement in accordance with the Deming Quality Process. The existence of these teams facilitated the success of the TUR teams.

In the case of the carbon dioxide substitution for sulfuric acid, plant personnel had observed carbon dioxide treatment of wastewater at another textile plant. This previous demonstration of the technology triggered the efforts at Cranston to implement such an operation. The innovative CO₂ delivery system was a technological hurdle which had to be overcome. Mutual engineering effort on the part of Cranston and the supplier of the carbon dioxide resulted in the successful design and production of a bench-scale unit prior to the implementation of the production unit.

5.3 Previous Successes with TUR Approach

Until the early 1980's, several environmental issues at Cranston were approached from an end-of-pipe perspective, with less than satisfactory resolution. The engineering group decided to take an innovative approach by targeting the operational source of the pollution. For example, in 1987, the Webster Division worked with the Department of Environmental Protection (DEP) to reduce emissions of volatile organic compounds (VOC's) primarily mineral spirits, and chose to use no-VOC or reduced-VOC color paste. This switch satisfied the DEP permitting team and allowed the implementation of a RACT (Reasonably Available Control Technology) Plan which Cranston could abide by. This substitution resulted in a significant reduction of byproducts and emissions and also reduced costs. These previous TUR successes helped shift the current engineering focus and management support towards TUR methodologies for reductions in cost, environmental impact, and worker exposure.

6.0 TRANSFERABILITY

Understanding the extent to which a manufacturing process is "under control" is the first step toward improving that process. All manufacturing processes which involve the use of toxic chemicals can employ control charting as a means to assess the efficiency of materials use. The information gathered on control charts can highlight areas needing improvements and thus reduce toxics use through process improvements. Acid aging of textiles is unique to azoic dyes; recovery of acid vapors, however, may be possible in a variety of processes if the properties of the acid are suitable. Operations which generate and treat alkaline wastewater can eliminate the use of neutralizing acid by substituting carbon dioxide as the pH neutralizing agent. Additionally, manufacturing operations which need to lower process pH may be able to eliminate the need for acid by substituting carbon dioxide to reduce alkalinity.

